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First Named Inventor	Henry Alfred Craddock
Group Art Unit	1712
Examiner Name	Not Yet Assigned
Attorney Docket Number	08830-0268 US1

Total Number of Pages in This Submission

## ENCLOSURES (check all that apply)

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Remarks

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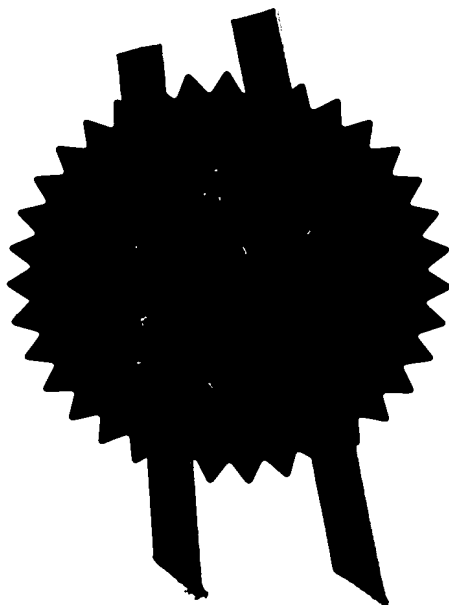
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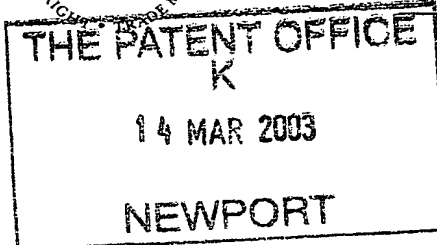
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# Request for grant of a patent

(See the notes on the back of this form. You can also get an explanatory leaflet from the Patent Office to help you fill in this form)

1. Your reference	P33729-/SGR/CWA		
2. Patent application number (The Patent Office will fill in this part)	0305862.5		14 MAR 2003
3. Full name, address and postcode of the or of each applicant (underline all surnames)  Patents ADP number (if you know it)  If the applicant is a corporate body, give the country/state of its incorporation	TR Oil Services Limited Howe Moss Place Kirkhill Industrial Estate Dyce Aberdeen AB2 0GL United Kingdom 858 7867001		
4. Title of the invention	"Method and Chemicals"		
5. Name of your agent (if you have one)  "Address for service" in the United Kingdom to which all correspondence should be sent (including the postcode)  Patents ADP number (if you know it)	Murgitroyd & Company  Scotland House 165-169 Scotland Street Glasgow G5 8PL  11980135		
6. If you are declaring priority from one or more earlier patent applications, give the country and the date of filing of the or of each of these earlier applications and (if you know it) the or each application number	Country	Priority application number (if you know it)	Date of filing (day / month / year)
7. If this application is divided or otherwise derived from an earlier UK application, give the number and the filing date of the earlier application	Number of earlier application		Date of filing (day / month / year)
8. Is a statement of inventorship and of right to grant of a patent required in support of this request? (Answer 'Yes' if: a) any applicant named in part 3 is not an inventor, or b) there is an inventor who is not named as an applicant, or c) any named applicant is a corporate body. See note (d))	Yes		

# Patents Form 1/77

Enter the number of sheets for any of the following items you are filing with this form. Do not count copies of the same document

Continuation sheets of this form

Description

15

Claim(s)

Abstract

Drawing(s)

10. If you are also filing any of the following, state how many against each item.

Priority documents

Translations of priority documents

Statement of inventorship and right to grant of a patent (Patents Form 7/77)

Request for preliminary examination and search (Patents Form 9/77)

Request for substantive examination (Patents Form 10/77)

Any other documents (please specify)

11.

I/We request the grant of a patent on the basis of this application.

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Murgitroyd & Co

Date

13/03/2003

Murgitroyd & Company

12. Name and daytime telephone number of person to contact in the United Kingdom

Craig Watson

01224 706616

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1     "Method and Chemicals"

2

3     This invention relates to a method and chemicals for  
4     inhibiting corrosion in an aqueous environment and  
5     particularly but not exclusively to the use of small  
6     organo-sulphur molecules such as thiohydantoins as  
7     corrosion inhibitors or corrosion inhibitor  
8     synergists in the oil industry.

9

10    Advances in drilling and completion technology have  
11    revolutionised new field development and the use of  
12    subsea wells with long tie backs is now common. The  
13    low temperatures and long fluid transport times  
14    under subsea conditions often result in a wide  
15    variety of production chemistry related problems,  
16    including corrosion, scale, wax and asphaltene  
17    deposition, hydrate formation and bacterial growth.

18

19    It is known that alkyl quaternary ammonium salts can  
20    be used as corrosion inhibitors and these are  
21    commercially available under the brand names such as  
22    Dodigen<sup>TM</sup> and Dodicon<sup>TM</sup>. It is thought that the

1 molecules of these salts attach to the downhole  
2 metal structure - normally via a nitrogen atom  
3 present in the molecule - and through a process of  
4 self-assembly provide a physical barrier or film  
5 between water and the structure. This film prevents  
6 corrosion of the structure because the water (which  
7 includes corrosion causing agents such as CO<sub>2</sub> and  
8 H<sub>2</sub>S) is prevented from contacting the structure.  
9 Also, the organic groups present in the inhibitors,  
10 being hydrophobic, repel water.

11

12 It is known that the addition of other chemicals,  
13 known as synergists, can significantly increase the  
14 effectiveness of the corrosion inhibitors. The  
15 synergists are thought to help the inhibitors bond  
16 with the metal structure to provide a more effective  
17 physical barrier to water.

18

19 The corrosion rates for some alkyl quaternary  
20 ammonium salt corrosion inhibitors used with and  
21 without synergists are shown in the table below. It  
22 is shown from these results that although the  
23 ammonium salt and the synergist reduce the corrosion  
24 rate moderately when used independently of each  
25 other, when used together their combination reduces  
26 the corrosion rate significantly.



chemical	corrosion rate
blank	32.87 mpy
5ppm thiosulphate	17.93 mpy
20ppm Dodigen 2808	17.46 mpy
20ppm Dodigen 2808+5ppm thiosulphate	0.61 mpy
20ppm Dodigen 179	27.40 mpy
20ppm Dodigen 179+5ppm thiosulphate	1.00 mpy

1

2 Thioacetamide ( $\text{CH}_3\text{CSNH}_2$ ) has been identified as a  
 3 persistent corrosion inhibitor/corrosion inhibitor  
 4 synergist. However, it is known as a possible  
 5 carcinogen and is therefore unsuitable for field  
 6 deployment.

7

8 Sodium thiosulphate (STS) and thioglycolic acid  
 9 (TGA) are also known corrosion inhibitors but suffer  
 10 from the disadvantages that the former can promote  
 11 pitting of stainless steels at high dose rates  
 12 whilst the latter is a toxic and stench chemical.

13

14 Substituted thiohydantoins are used in the  
 15 identification of the N-terminal amino acid units of  
 16 a peptide chain by means of the Edman Degradation.

17

18 A free amine function bonds to a phenyl  
 19 isothiocyanate reagent and produces a thiohydantoin  
 20 hetrocycle incorporating the N-terminal amino acid  
 together with a shortened peptide chain.

21

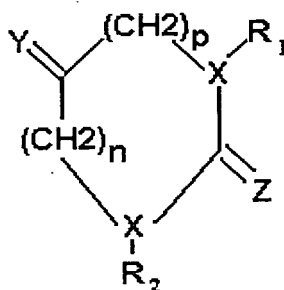
22 Characteristic hydantoin derivatives of all the  
 23 amino acids have been catalogued so identification  
 of the terminal units is accomplished by comparison.

24

25 Thiohydantoins are commercially available from  
 26 Sigma-Aldridge and other chemical suppliers.

Thiohydantoin is not carcinogenic.

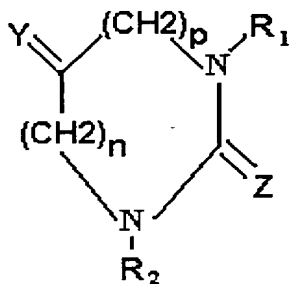
According to a first aspect of the present invention, there is provided a method of inhibiting corrosion in an aqueous environment, the method comprising the step of injecting a chemical according to the following formula into an aqueous environment:-



wherein n is any number between 1 and 100, p is any number between 0 and 100, R<sub>1</sub> is H or an organic group, R<sub>2</sub> is H or an organic group, and X, Y and Z are independently any suitable atom or functional group.

Preferably, X is a nitrogen atom or alternatively a phosphorus atom. Preferably Y is an oxygen atom or alternatively a S atom. Preferably Z is a sulphur atom or alternatively an O atom.

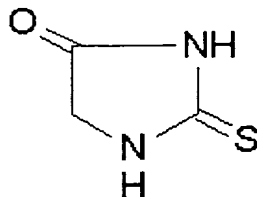
Preferably the chemical comprises a structure according to the following formula:-



1  
2 Preferably P is of the value of 0 or 1. Where P is  
3 greater than or equal to one, the C<sub>p</sub> atom typically  
4 bonds to the C<sub>y</sub> atom and to the X atom or functional  
5 group; there is typically no covalent bond between  
6 the C<sub>y</sub> atom and the X atom or functional group.  
7 Where P is zero there is typically a covalent bond  
8 between the C<sub>y</sub> atom and the X atom or functional  
9 group.

10  
11 Preferably the value of n is 1 or 2, more preferably  
12 1.

13  
14 Preferably, the chemical is 2-thiohydantoin, as  
15 represented by the following formula:-



17  
18  
19 Preferably, the aqueous environment is an oilfield  
20 environment.

21

1 The aqueous environment may be any one of a cooling  
2 water system, a water flood system and a produced  
3 water system. The aqueous environment may also be  
4 in crude oil systems or gas systems and may be  
5 deployed downhole, topside, pipeline or during  
6 refining.

7  
8 The aqueous environment may include  $\text{CO}_2$ ,  $\text{H}_2\text{S}$ ,  $\text{O}_2$ ,  
9 brine, condensed water, crude oil, gas condensate,  
10 or any combination of the said or other species.

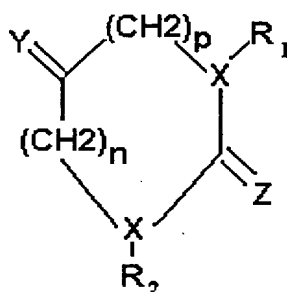
11  
12 The chemical may be deployed continuously or  
13 alternatively as a batch. The chemical may be used  
14 in low or high shear conditions.

15  
16 The chemical may be used as a corrosion inhibitor or  
17 as a corrosion inhibitor synergist in combination  
18 with an organic corrosion inhibitor. Examples of  
19 oilfield corrosion inhibitors for which synergists  
20 are useful include amines, amido amines,  
21 quatazamines, imidazolines, amides, ethoxylated  
22 amines, quaternary ammonium salts, betaines,  
23 phosphate esters, sulphonates, polyaspartates, as  
24 part of a combined product, i.e. corrosion inhibitor  
25 combined with scale inhibitor, wax inhibitor,  
26 hydrate inhibitor, demulsifier, deoiler or any other  
27 corrosion inhibitor. Oligomers and polymers of  
28 these corrosion inhibitors may also be used with the  
29 chemical.

30  
31 When used as a synergist,  $R_1$  and  $R_2$  are preferably  
32 organic groups such as alkyl groups. Preferably  $R_1$

1 and R<sub>2</sub> comprise between 1 and 40 carbon atoms, more  
2 preferably around 18 carbon atoms.

3  
4 According to a second aspect of invention, there is  
5 provided a chemical for use as a corrosion  
6 inhibitor, or as a corrosion inhibitor synergist,  
7 the chemical being represented by the following  
8 formula:-

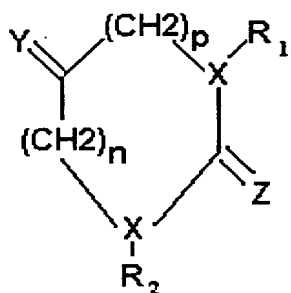


9  
10 wherein n is any number between 1 and 100, p is  
11 any number between 0 and 100, R<sub>1</sub> is H or an organic  
12 group, R<sub>2</sub> is H or an organic group, and X, Y and Z  
13 are independently any suitable atom or functional  
14 group.

15  
16 Preferably the chemical of the second aspect of the  
17 invention is used for the method according to the  
18 first aspect of the invention.

19  
20 Preferably the chemical of the second aspect of the  
21 invention is the chemical as described with respect  
22 to the first aspect of the invention.

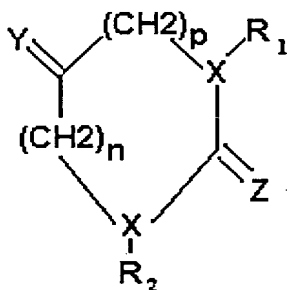
23  
24 The invention also provides the use of a chemical of  
25 the following formula



wherein n is any number between 1 and 100, p is any number between 0 and 100, R<sub>1</sub> is H or an organic group, R<sub>2</sub> is H or an organic group, and X, Y and Z are independently any suitable atom or functional group;

as a corrosion inhibitor or as a corrosion inhibitor synergist.

The invention also provides a corrosion inhibitor or corrosion inhibitor synergist, comprising a chemical of the following formula



wherein n is any number between 1 and 100, p is any number between 0 and 100, R<sub>1</sub> is H or an organic group, R<sub>2</sub> is H or an organic group, and X, Y and Z

1 are independently any suitable atom or functional  
2 group.

3 Embodiments of the invention will now be described  
4 by way of example only.

5

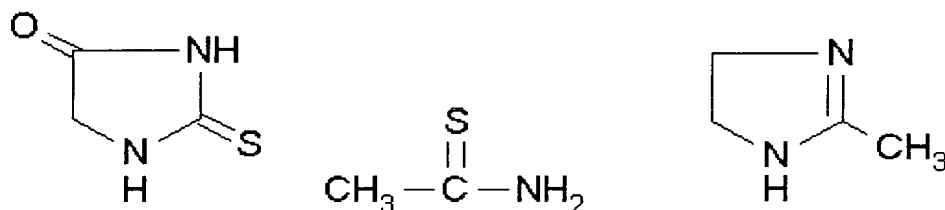
6 In order to investigate the efficiency of corrosion  
7 inhibition by thiohydantoin, aqueous linear  
8 polarisation resistance (LPR) bubble tests were  
9 carried out and compared with thioacetamide.

10 Thiohydantoin is not carcinogenic. As the basic  
11 structure of thiohydantoin is related to imidazoline  
12 it was also compared against 2-methyl-2-imidazoline  
13 a similar sulphur free imidazoline.

14

15 The structures of 2-thiohydantoin, thioacetamide and  
16 2-methyl-2-imidazoline are shown below:-

17



18

19 2-thiohydantoin thioacetamide 2-methyl-2-imidazoline

20

21 The procedure for conducting the bubble test is  
22 generally based on a protocol developed by BP  
23 Sunbury and described in "Corrosion Inhibitor Test  
24 Methods", S Webster, A J McMahon, D M E Paisley, D  
25 Harrop, BP Sunbury report ESR.94.ER.054, dated  
26 November 1996 and also "Corrosion Inhibitor  
27 Guidelines", A J McMahon, S Groves, BP Sunbury  
28 report ESR.95.ER.050, dated 1996.

The procedure also makes use of principles from the following ASTM standards,

- G1-90 (1999) "Standard Practise for Preparing, Cleaning and Evaluating Corrosion Test Specimens"

- G102-89 (1999) "Standard Practice for Calculation of Corrosion Rates and Related Information from Electrochemical Measurements"

- G5-94 (1999) "Test Method for Making Potentiostatic and Potentiodynamic Anodic Polarization Measurements"

- G59-97 "Standard Practice for Conducting Potentiodynamic Polarization Resistance Measurements"

- G61-86 (1998) "Standard Test Method for Conducting Cyclic Potentiodynamic Polarization Measurements for Localized Corrosion Susceptibility of Iron-, Nickel-, or Cobalt-Based Alloys".

The bubble test comprises a carbon steel electrode immersed in a bath of oilfield brine and possibly a crude oil to simulate the environment in which the corrosion inhibitor would be used. A gas, commonly CO<sub>2</sub> which is a corrosion causing agent, is bubbled through the brine mixture and the corrosion rate of the electrode in the absence of a corrosion inhibitor is measured using the linear polarisation



resistance method (LPR) or AC Impedance (EIS). The inhibitor under examination is then added, normally after two hours, and the subsequent polarisation resistance/ corrosion rate is recorded. This data can be used to calculate the inhibitor efficiency.

## Results

Aqueous bubble tests were carried out on the three inhibitors/synergists in duplicate.

Inhibitor	Dose (ppm)	Corrosion Rate (mpy)		% Inhibition
		Before inhib.	After inhib.	
thioacetamide	1	144.96	5.58	96.15
thioacetamide	1	152.60	3.55	97.67
thiohydantoin	1	163.47	18.07	88.95
thiohydantoin	1	141.09	9.42	93.32
2-methyl-2-imidazoline	1	146.81	216.65	0
2-methyl-2-imidazoline	1	144.07	193.81	0

**Table 1 : Aqueous Bubble Test Results using 3% NaCl at 50°C**

In these tests the thiohydantoin did not perform as well as thioacetamide. Methyl imidazoline performed poorly as the corrosion rate actually increased, from 145mpy to 200mpy and therefore it was decided not to continue testing with this product.

The aqueous bubble tests were repeated using BP Forties synthetic brine and the results are shown in table 2. In this test the performances of

thioacetamide and thiohydantoin had improved with a dramatic improvement in the result from thiohydantoin when compared to the bubble test with 3% NaCl.

Inhibitor	Dose (ppm)	Corrosion Rate (mpy)		% Inhibition
		Before inhib.	After inhib.	
Thioacetamide	1	146.84	1.29	99.12
Thioacetamide	1	208.29	0.82	99.61
Thiohydantoin	1	174.73	1.64	99.06
Thiohydantoin	1	132.10	1.07	99.19

**Table 2 : Aqueous Bubble Test Results using Forties Synthetic Brine at 50°C**

Partition bubble tests were performed on thioacetamide and thiohydantoin. In this test 600ml of brine is first added to a test cell. A mixture of a further 200 ml brine and 200 ml crude oil is made up and thoroughly mixed before being added to the brine in the test cell.

The fluids used in the partition bubble tests were Forties synthetic brine and Forties crude oil. 800ml of brine and 200ml of crude were used to investigate the partition efficiency of the inhibitors/synergists and the results are shown in table 3 below.

Inhibitor	Dose (ppm)	Corrosion Rate (mpy)		% Inhibition
		Before inhib.	After inhib.	
Thioacetamide	1	241.36	0.97	99.60
Thioacetamide	1	211.37	0.70	99.67

Thiohydantoin	1	239.59	2.41	98.99
Thiohydantoin	1	202.79	1.35	99.33

**Table 3 : Partition Bubble Test Results using  
Forties Synthetic Brine at 50°C**

The performance of thioacetamide and thiohydantoin was similar to that achieved under aqueous Forties conditions. (Table 2)

Thiohydantoin was evaluated further as a corrosion inhibitor and as a corrosion inhibitor synergist using a rotating cylinder electrode (RCE) at 5000rpm (29.5 Pa). The rotating cylinder electrode test comprises a rotating carbon steel electrode immersed in a bath of oilfield brine and possibly crude oil to simulate the shear stresses that may be encountered in the environment which the corrosion inhibitor would be used. In certain tests, pre-partitioning of the inhibitor is carried out with brine/crude shaken with inhibitor present and the separated brine used for the tests. A gas, commonly CO<sub>2</sub>, is bubbled through the brine mixture and the electrode rotation started at the required rate. The corrosion rate of the brine is then measured using the linear polarisation resistance method and/or AC impedance. If unpartitioned brine is used the inhibitor being tested is added at this point and the inhibitor rate measured. If partitioned brine is used the initial rate is the inhibitor corrosion rate and is compared to partitioned brine without inhibitor to calculate the inhibition ratio.

The results are shown in Table 4.

Inhibitor	Dose (ppm)	Corrosion Rate (mpy)		% Inhibition
		Before inhib.	After inhib.	
thiohydantoin	1	160.50	4.65	97.10
thiohydantoin	1	90.01	11.24	87.51
thiohydantoin(1ppm) + QUAT(2ppm)	3	91.76	2.80	96.95
thiohydantoin(1ppm) + QUAT(2ppm)	3	90.06	5.59	93.79

**Table 4 : Rotating Cylinder Electrode Test using  
3%NaCl Brine at 50°C**

The quantity of thiohydantoin used in the formulation with the QUAT is the same as in previous tests. The QUAT is CLARIANT<sup>TM</sup> Dodigen 2808, a coco benzyl quat.

A further RCE test was used to investigate the persistency of thiohydantoin. The brine was replaced with fresh brine after 20 hours. Although some persistency was observed the corrosion rate increased from 11mpy to 35 mpy and the results are shown in Table 5.

Inhibitor	Dose (ppm)	Corrosion Rate (mpy) % Inhibition		
		Before inhib.	After inhib.	Fresh brine
Thiohydantoin	1	90.01	11.25	35.45

**Table 5 : Persistency Test using 3%NaCl Brine at  
50°C**

1 On the basis of these tests thiohydantoin is a  
2 viable and non-carcinogenic alternative to  
3 thioacetamide. Thiohydantoin matches the excellent  
4 corrosion inhibition of thioacetamide in a series of  
5 static and dynamic tests. Indeed, it is considered  
6 that thiohydantoin is suitable to be used as a  
7 corrosion inhibitor in its own right rather than  
8 simply as a synergist for known corrosion  
9 inhibitors. In such cases, the hydrogens attached  
10 to the nitrogen atoms may be replaced by organic or  
11 alkyl groups of the order of  $C_1$ - $C_{40}$  but preferably  
12 around  $C_{18}$ .

13  
14 A six membered ring equivalent such as a pyrimidine  
15 based ring is also effective against corrosion  
16 inhibition.

17 Thiohydantoin (and derivatives) are also effective  
18 against other known corrosion causing agents, such  
19 as  $H_2S$ .

20

21 Modifications and variations may be made without  
22 departing from the scope of the invention.

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